GROUP-THEORETICAL CLASSIFICATION OF THE STATES OF PAIRS AND COMPLEXES OF IMPURITY PARAMAGNETIC IONS IN CRYSTALS

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Abstract

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GROUP-THEORETICAL CLASSIFICATION OF THE STATES OF PAIRS AND COMPLEXES OF IMPURITY PARAMAGNETIC IONS IN CRYSTALS

In a previous article by the authors ([1]), a group-theoretical method was proposed for determining the allowed terms of a pair of bound impurity ions in a crystal. In the present article this method is generalized to a symmetric complex of N impurity ions in an ionic crystal. In addition, some inaccuracies of the preceding article are eliminated.

If covalent effects are neglected, then the electrons of the filled shells of nonimpurity ions are immaterial for the classification of the states of the complex.* Therefore let us consider the Hamiltonian of a system of electrons belonging only to the unfilled shells of N impurity paramagnetic ions:

$$H = \sum_{i=1}^{N} H_0(i) + \sum_i \sum_{j \neq i} \bar{V}_j(i) + V_{ee} + \sum_i V_{\text{cr.env}}(i), \tag{1}$$

where $H_0(i)$ is the Hamiltonian of the i-th free impurity ion; $\bar{V}_j(i)$ is the energy of the i-th impurity ion in the field produced by the nucleus (and the filled electron shells) of the j-th impurity ion; V_{ee} is the energy of interaction of electrons of different impurity ions with one another; and $V_{\text{cr.env}}(i)$ is the energy of the i-th impurity ion in the crystal field produced by the matrix ions surrounding the impurity complex.

The first three terms in (1) have the symmetry G_C^m of the "impurity molecule" (with a "center" at some point C), while the last term has the symmetry G_C of the crystal field produced by the crystal with "holes" at the sites occupied by substitutional impurity ions (the symmetry of the environment of the complex). Therefore we shall define the symmetry group G_k of the complex in the crystal as the intersection of the groups:

$$G_k = G_C^m \cap G_C \tag{2}$$

(for a pair $D_C^m = D_{\infty h}$ or $C_{\infty v}$).

In the Hamiltonian (1) one can always single out a zeroth-approximation term** $\sum_i [H_0(i) + V_{\text{cr}}(i)]$, adding and subtracting the corresponding summands, where $V_{\text{cr}}(i)$ is the energy of the impurity ion in the crystal field produced by the principal ions of the crystal. This term has the symmetry $G_1 \times G_2 \times \cdots \times G_N$ (G_i is the point symmetry group of the i-th ion in the absence of other impurity ions). We shall start from the specified states $\alpha_i \Gamma_i$ of the impurity ions in the crystal field with symmetry G_i (including spin-orbit interaction). Here Γ_i is an irreducible representation of the group G_i, and α_i are additional quantum numbers.

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* Consideration of covalent effects in our scheme is possible, for example, by including in the complex under consideration, besides impurity ions, also the ligands nearest to them and taking account of all ionic and covalent structures of such a complex.

** For classification of a state, the order of magnitude of the various terms of the Hamiltonian is not important.

Let us denote the wave function of ion A_i by $\psi_{A_i t_i a_i \Gamma_i \mu_i}(q_i)$, where t_i is the ion type (taking into account its species and crystal environment); μ_i is a "row" of the representation Γ_i; q_i is the set of Cartesian and spin coordinates of all n_i electrons of ion A_i.

To each element $g \in G_k$ there corresponds a certain permutation of impurity ions, which can always be represented as a product of cyclic permutations $g \to P_g = P_g(A_1, A_2, \ldots, A_m) \ldots$ (the dots at the end denote other cyclic permutations). Thus, for each g all impurity ions are naturally distributed into sets—cycles.

The antisymmetric wave functions of the states of the complex (in the zeroth approximation), belonging to the eigenvalue $\sum_i E^{(0)}(A_i t_i a_i \Gamma_i)$, can be written in the form

$$\Psi_{A_1 t_1 a_1 \Gamma_1 \mu_1 \ldots A_m t_m a_m \Gamma_m \mu_m; \ldots}(q_1 \ldots q_m; \ldots) = \sum_{\mathcal{P}} (-1)^{\mathcal{P}} \mathcal{P}\, \psi_{A_1 t_1 a_1 \Gamma_1 \mu_1}(q_1) \ldots \psi_{A_m t_m a_m \Gamma_m \mu_m}(q_m) \ldots, \tag{3}$$

where $\mathcal{P}$ are the operators of all possible permutations of electron coordinates between impurity ions (it is clear that only equivalent ions can enter one and the same cycle, i.e., ions of the same type $t_1 = t_2 = \cdots = t_m = t; \ldots$). We note that the set of wave functions (3) can be divided into separate sets that differ from one another by all possible permutations of unequal states among equivalent ions (including those from different cycles). These permutations take into account the expression for the exchange of states between equivalent ions.

Each set contains also $[\Gamma_1][\Gamma_2]\dots[\Gamma_N]$ functions, differing from one another by the values $\mu_1, \mu_2, \dots, \mu_N$ ($[\Gamma_i]$ is the dimension of the representation Γ_i).

The wave functions of the ions are each defined in its own local coordinate system K_i. Having chosen the local coordinate system K_1 of ion A_1 of the first cycle, one may choose the local coordinate systems of the remaining ions, for example, by the action of the operator $\hat{g}$: $K_2 = \hat{g}K_1$, $K_3 = \hat{g}K_2, \dots, K_m = \hat{g}K_{m-1}$ (analogously for other cycles). We note that with such a choice $K_1 = \hat{g}^{-m}\cdot\hat{g}\cdot K_m$, i.e., in the case when $\hat{g}^m \neq E$, we have $K_1 \neq \hat{g}K_m$. It is not difficult to show that, with our choice of local coordinate systems, the action of the element $\hat{g}$ on the wave functions of the ions reduces to the following:

$$\hat{g}\psi_{A_i t_i a_i \Gamma_i \mu_i}(q_i) = \psi_{A_{i+1} t_i a_i \Gamma_i \mu_i}(q_i) \qquad \text{for } i = 1, 2, \dots, m-1,$$

$$\hat{g}\psi_{A_m t_m a_m \Gamma_m \mu_m}(q_m) = \hat{g}^m \psi_{A_1 t a_m \Gamma_m \mu_m}(q_m) \qquad \text{for } i = m. \tag{4}$$

Let us now consider the action of the element $\hat{g}$ on the functions (3) and, taking the set (3) as a basis of a representation of the group G_k, derive formulas for determining the characters of this representation. Using (4), we find*

$$\hat{g}\Psi_{A_1 t a_1 \Gamma_1 \mu_1 \dots A_m t a_m \Gamma_m \mu_m;\dots}(q_1 \dots q_m; \dots) =$$

$$= \sum_{\mathcal{P}} (-1)^{\mathcal{P}} \mathcal{P} \left[\sum_{\mu'_m} D^{(\Gamma_m)}_{\mu'_m \mu_m}(\hat{g}^m) \hat{P}_g(A_1 A_2 \dots A_m)\, \psi_{A_1 t a_1 \Gamma_1 \mu_1}(q_1) \dots \right.$$

$$\left. \dots \psi_{A_m t a_m \Gamma_m \mu'_m}(q_m) \right] \dots$$

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* Here it is taken into account that the element g^m returns all ions of the cycle to their initial positions, i.e., this element must be present in each of the equivalent point groups $G_1, G_2, \dots, G_m$.

The antisymmetric wave function will not change if the coordinate permutation operator $P_g(q_1 q_2 \dots q_m)$ is applied to it and this function is simultaneously multiplied by $\pi^n = (-1)^{wn}$, where n is the number of electrons in each of the ions of the cycle, and w is the parity of the cyclic permutation P_g. Analogous operations must be performed for the other cycles. As a result, taking also into account that application of the operator $P_g(A_1 A_2 \dots A_m) \cdot P_g(q_1 q_2 \dots q_m)$ in our case is equivalent to application of the operator $P_g^{-1}(a_1 \Gamma_1 \mu_1, a_2 \Gamma_2 \mu_2, \dots, a_m \Gamma_m \mu'_m)$, we obtain:

$$\hat{g}\Psi_{A_1 t\alpha_1\Gamma_1\mu_1\ldots A_{mt}\alpha_m\Gamma_m\mu_m;\ldots}(q_1\ldots q_m;\ldots)=[\pi^n\ldots]\left[\sum_{\mu'_m}D^{(\Gamma_m)}_{\mu'_m\mu_m}(g^m)\ldots\right]\times$$

$$\times\left[P_g^{-1}(a_1\Gamma_1\mu_1,\ldots,a_m\Gamma_m\mu'_m)\ldots\right]\Psi_{A_1 t\alpha_1\Gamma_1\mu_1\ldots A_{mt}\alpha_m\Gamma_m\mu'_m;\ldots}(q_1q_2\ldots q_m). \quad (5)$$

If, in at least one of the cycles, not all $a_i\Gamma_i\mu_i$ are identical, then the original function will not enter the right-hand side of (5), since the states $a_i\Gamma_i$ of the ions are cyclically permuted under the action of the operator P_g^{-1}. Therefore the contribution to the character of those sets of functions from (3) to which unequal states $a_i\Gamma_i\mu_i$ of the ions correspond, in at least one of the cycles, will be equal to zero. The remaining sets give the character

$$X(g)=[\pi^n\ldots\bar{\pi}^{\bar{n}}]\sum_{\text{over sets}}{}'X^{(\Gamma)}(g^m)\ldots X^{(\bar{\Gamma})}(\bar{g}^{\bar{m}}). \quad (6)$$

(the quantities pertaining to the last cycle are marked with a bar above), where the summation extends over all sets, and the prime denotes the condition

$$a_1\Gamma_1=a_2\Gamma_2=\ldots=a_m\Gamma_m=a\Gamma;\ \ldots;\ \bar{a}_1\bar{\Gamma}_1=\bar{a}_2\bar{\Gamma}_2=\ldots=\bar{a}_{\bar{m}}\bar{\Gamma}_{\bar{m}}=\bar{a}\bar{\Gamma}.$$

(If there are no sets satisfying this condition, the character is zero.)

In the particular case of elements of the type $g=g^0$, where g^0 is an element to which the permutation $P_g=1$ corresponds, from (6) we obtain

$$X(g^0)=\sum_{\text{over sets}}X^{(\Gamma_1)}(g_1^0)\ldots X^{(\Gamma_N)}(g_N^0), \quad (7)$$

where $g_1,g_2,\ldots,g_N$ are the "record" of the element g in each of the point groups $G_1,G_2,\ldots,G_N$, respectively. In this case each of the ions of the complex forms a separate cycle.

If the group G_k is decomposed with respect to the invariant subgroup* G_k^J (which includes only elements of the type g^0),

$$G_k=G_k^J+I_1G_k^J+\ldots+I_sG_k^J,$$

then each element $g\in G_k$ can be represented in the form $g=Ig^0$ (where I is an element not belonging to G_k^J), and formula (6) in the form

$$X(Ig^0)=[\pi^n\ldots\bar{\pi}^{\bar{n}}]\sum_{\text{over sets}}{}'X^{(\Gamma)}(I^m g_1^0g_2^0\ldots g_m^0)\ldots X^{(\bar{\Gamma})}(I^{\bar{m}}\bar{g}_1^0\bar{g}_2^0\ldots\bar{g}_{\bar{m}}^0). \quad (8)$$

For a complex of two equivalent impurity ions (a pair), from (6)-(8) we obtain:

$$X(g^0)=\begin{cases}X^{(\Gamma)}(g_1^0)X^{(\Gamma)}(g_1^0), & \text{if } a_1\Gamma_1=a_2\Gamma_2;\\ X^{(\Gamma_1)}(g_1^0)X^{(\Gamma_2)}(g_2^0)+X^{(\Gamma_2)}(g_1^0)X^{(\Gamma_1)}(g_2^0), & \text{if } a_1\Gamma_1\neq a_2\Gamma_2;\end{cases} \tag{9a}$$

$$X(g)=X(Ig^0)=\begin{cases}(-1)^nX^{(\Gamma)}(g^2)=(-1)^nX^{(\Gamma)}(I^2g_1^0g_2^0), & \text{if } a_1\Gamma_1=a_2\Gamma_2,\\ 0, & \text{if } a_1\Gamma_1\neq a_2\Gamma_2.\end{cases} \tag{9b}$$

* For a pair of impurity ions in such a decomposition there will be two cosets, and in the general case more.

It is seen from (96) that in formula (3) of paper ([1]), under the character sign, the quantity I^2 was omitted. In the case when $I^2=Q$ (rotation by 2π) (for example, for $I=C_2$), this is important for double-valued representations Γ (Q changes the sign of the character). In connection with this, the following corrections must be made in Table 1 of article ([1]): $\overline{2A}\times\overline{2A}\to 3A_1+A_2$ (pair I) and $3A+B$ (pair III), and also $\overline{E}\times\overline{E}\to 2A_1+E$ (pair I) and $3A+B$ (pair III). In addition, the misprint $\overline{E}\times\overline{E}\to A_g+A_u+E_u$ (pair V) should be corrected.

Examples of determining the states of complexes with $N>2$ will be considered by the authors separately.

We note that the proposed method is also applicable to free polyatomic molecules if one sets $G_C=R_C$ and $G_i=R_i$ (R is the rotation group). In this case our method differs from that proposed by Kotani ([2]) in that the spin-orbit interaction is taken into account from the very beginning.

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Note: Figure translations are in progress. See original paper for figures.